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DEPARTMENT OF  
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**ChT – 03014**  
**CHEMICAL TECHNOLOGY I**

B.Tech ( First Year )

Chemical Engineering

# PART 1

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# Chapter 1

## Water Conditioning and Environmental Protection

Water conditioning and wastewater treatment have long been essential functions of municipalities. However, the importance of suitably preparing water for the chemical industry is now fully recognized. Industrial wastewaters present a complex and challenging problem to the chemical engineer. Besides moral and community considerations, laws prohibiting and limiting the pollution of streams and air require these problems to be considered as a necessary operating expense. Although the solution is specific with each industry (indeed, almost with each plant or factory), a few general principles may be observed: increasing reuse of wastewaters, control of pollution and, if feasible, recovery of by-products at their source to lessen the expense of treatment, and lagooning of wastes to keep pollution at a minimum level or to effect a saving in neutralization costs.

As is well known, the quality and the quantity of available water are very important in choosing the location of a chemical plant. Both the surface water and the groundwater should be considered. The latter is usually more suitable for cooling purposes because of the fairly constant temperatures during the summer and winter, but such water is generally harder, may cause scale, which may interfere with heat transfer. The impurities contained in water vary greatly from one section of the country to another. Hard waters are those containing objectionable amounts of dissolved salts of calcium and magnesium. These are usually present as bicarbonates, chlorides, sulfates, and nitrates. These salts give insoluble precipitates with soap, and calcium sulfate, carbonate, and silicate form clogging scales with low thermal conductivity in boilers. Magnesium silicate, as well as calcium carbonate, may reduce heat transfer in process heat exchangers.

Although, on an average day,  $1.6 \times 10^{10}$  m<sup>3</sup> of water falls on the United States (75 cm/year average), of which 70 percent is recycled to the atmosphere by evaporation or transpiration of plants, the increasing growth of population and of industry makes for local shortages. The amount of water used in the United States in 1960 amounted to  $1.18 \times 10^9$  m<sup>3</sup>/day and in 1980,  $2.11 \times 10^9$  m<sup>3</sup>/day. The total supply of fresh water available in the United States has been estimated at  $2.46 \times 10^9$  m<sup>3</sup>/day, so it is obvious that demand is rapidly overtaking the supply.

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<sup>1</sup>*Water Quality and Treatment, A Handbook of Public Water Supplies*, American Water Works Assoc., 3d ed., McGraw-Hill, New York, 1971. Chanlett, *Environmental Protection*, McGraw-Hill, New York, 1973.

The problems<sup>2</sup> of quantity, quality, reuse, and pollution are complex and usually require expert study to decide between alternative sources of water and optimum treatment to minimize total cost of use. The decision generally depends on the use, whether for power generation, heating, cooling, or actual incorporation into a product or its manufacturing process.

Hardness is usually expressed in terms of the dissolved calcium and magnesium salts calculated as calcium carbonate equivalent. Water hardness may be divided into two classes: *carbonate* and *noncarbonate*, known as *temporary* and *permanent*. Temporary hardness can usually be greatly reduced by heating; permanent hardness requires the use of chemical agents. Carbonate, or temporary hardness, is caused by bicarbonates of calcium and magnesium; noncarbonate, or permanent hardness, is due to the sulfates and chlorides of calcium and magnesium. In addition to hardness, varying amounts of sodium salts, silica, alumina, iron, or manganese may also be present. The total dissolved solids may range from a few parts per million in snow water to several thousand parts per million in water from mineral springs. A water that contains even 1000 parts per million dissolved solids is considered to be a relatively poor quality water even though it is 99.9% pure. In the United States hardness is expressed as if all the hardness were due to calcium carbonate. The common units used in expressing water analyses are parts per million (ppm), grains per gallon (gr/gal), and milligrams per liter (mg/L). One grain per gallon is equivalent to 17.1 ppm and 17.1 mg/L. Other water impurities that may be present are suspended insoluble matter (classed usually as turbidity), organic matter, color, and dissolved gases. Such gases are free carbon dioxide, oxygen, nitrogen, and, in sulfur waters, hydrogen sulfide.

Approximately  $5 \times 10^8 \text{ m}^3$  ( $133 \times 10^9 \text{ gal}$ ) of municipal wastewater is reused for agriculture, cooling and process water, and nonpotable domestic applications. Industry may withdraw large quantities of water from the original source and use it in varied ways, but it actually consumes relatively little,<sup>3</sup> so that most of the water is returned to the source for reuse by others. The U.S. Department of Commerce has estimated that the average chemical process industry plant that had recycle rates of 2:1 to 5:1 just a few years ago is expected to reach 1:1 (pulp and paper), 27:1 (chemicals), and 40:1 (petroleum refining) by the year 2000. The recycle rate is the ratio of gross water use to intake. In many areas, treated sewage effluent is of a better quality than the natural water supply and, with improved waste treatment, industrial reuse becomes more and more feasible. Roughly 70 percent of all industrial water is used for cooling. Industrial reuse helps to reduce the chemical, thermal, and resultant biological stream pollution and brings the handling of water more under the direct control of the plant manager. Table 3.1 shows the trends in industrial reuse.

## WATER CONDITIONING

Water conditioning must be adapted to the particular use for which the water is designed, and problems should be referred to the experts in this field. The use of elevated pressures

<sup>2</sup>American Water Works Association *Water Control and Treatment*, 3d ed., McGraw-Hill, New York, 1971; Spiegler, *Salt Water Purification*, Plenum, New York, 1977.

<sup>3</sup>Water Reuse: A Trickle Becomes a Torrent, *Chem. Eng.* 85 (10) 44 (1978); *Water Reuse Studies*, API Publication 949, Washington, D.C., Aug. 1977; Foster and Barkely, *Water Reuse in the Southwest*, AIChE Symposium Series, vol. 73, no. 166, p. 183 1977; Holiday, *Conserving and Reusing Water*, *Chem. Eng.* 89 (8) 118 (1982).

**Table 3.1** Water-Use Patterns in the United States\*  
( $10^6 \text{ m}^3/\text{day}$ )

	Gross Use	Intake	Consumption	Total Discharge
1975				
Pulp and paper	110	38	3.8	34
Petroleum	95	19	3.8	15
Chemical and allied products	166	80	3.8	76
Total manufacturing	580	260	3.6	235
1985				
Pulp and paper	163	26	7.5	15
Petroleum	110	7.5	3.8	3.8
Chemical and allied products	310	23	7.5	15
Total manufacturing	860	102	38	64
2000				
Pulp and paper	261	23	19	3.8
Petroleum	155	3.8	3.8	>2
Chemical and allied products	602	23	15	3.8
Total manufacturing	1404	87	64	2.3

\*Data are rounded.

SOURCE: U.S. Dept. of Commerce

(17.2 MPa and higher for steam generation) requires the employment of extremely carefully purified boiler feedwater. Each industry has its special water-conditioning requirement; e.g., laundries require zero hardness to prevent the precipitation of calcium and magnesium soap on clothes. Calcium, magnesium, and iron salts cause undesirable precipitates with dyes in the textile industries and with the dyes in paper manufacture.

**HISTORICAL.** In this country an abundance of fairly soft water has long been available from surface supplies of the industrial Northeast. Cities such as New York and Boston obtain comparatively soft water from rural watersheds over igneous rocks. However, as the Middle West and the West were developed, it became necessary to use the harder water prevailing in many areas, particularly those rich in limestone. This hard water needs to be softened for many uses. Furthermore, as the advantages of really soft water are recognized, more and more fairly soft waters are being *completely softened* for laundries, homes, textile mills, and certain chemical processes. Thomas Clark of England, in 1841, patented the lime process for the removal of carbonate, or temporary hardness, followed by Porter, who developed the use of soda ash to remove the noncarbonate, or permanent, hardness of water. In 1906, Robert Gans, a German chemist, applied zeolites to commercial use for water-softening purposes. Only since the 1930s has softening been extended to municipal supplies to any appreciable extent. Figure 3.1 shows in a general way the variations in hardness of waters.

**METHODS.** The purification and softening of water may be accomplished by different methods, depending on the prospective use. *Softening* is the term applied to processes which remove or reduce the hardness of water. *Purification*, as distinguished from softening, usually refers to the removal of organic matter and microorganisms from water. *Clarification* may be very important and may be combined with cold-water softening by precipitation.

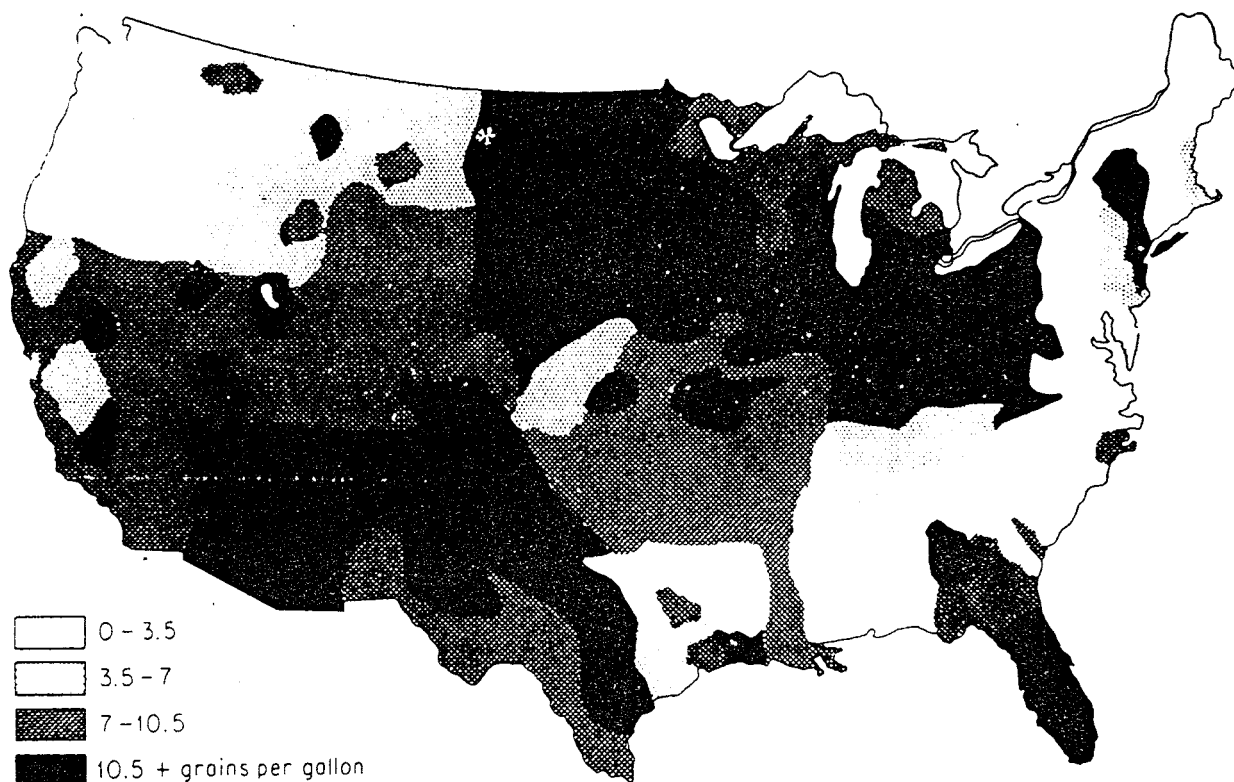


Fig. 3.1. A hard-water map of the United States shows that few parts have soft water (white areas). Most of the country has water of varying hardness (gray and black areas).

**Ion Exchange.** In 1852, Way discovered that the removal of ammonia from aqueous liquids passing through certain soils was really an exchange with the calcium of a particular type of silicate occurring in the soils. The real stimulus for organic exchange resins came when Adams and Holmes<sup>4</sup> published their paper on purely synthetic organic exchange resins and described anion-exchange resins. Now ion exchange has become a valuable chemical conversion process. Its utilization on a large industrial scale is widespread, including the commercial production of demineralized water having low electrical conductivity. Ion exchange is really a chemical reaction in which mobile hydrated ions of a solid are exchanged, equivalent for equivalent, for ions of like charge in solution. The solid has an open fishnetlike structure, and the mobile ions electrically neutralize charged, or potentially charged, groups attached to the solid matrix, called the ion exchanger. Cation exchange occurs when the mobile, positively charged cation fixed to the negatively charged fixed group of the ion exchanger, exchanges for another cation in the solution. Likewise, anion exchange occurs when the mobile, negatively charged anion attached to the positively charged fixed group on the ion exchange resin is exchanged for another anion in the solution.<sup>5</sup>

The first products used industrially for ion exchange were naturally occurring inorganic zeolites, such as aluminum silicates, which have very low exchange capacity per cubic meter of the material. The next improvement was the introduction of organic ion exchangers which

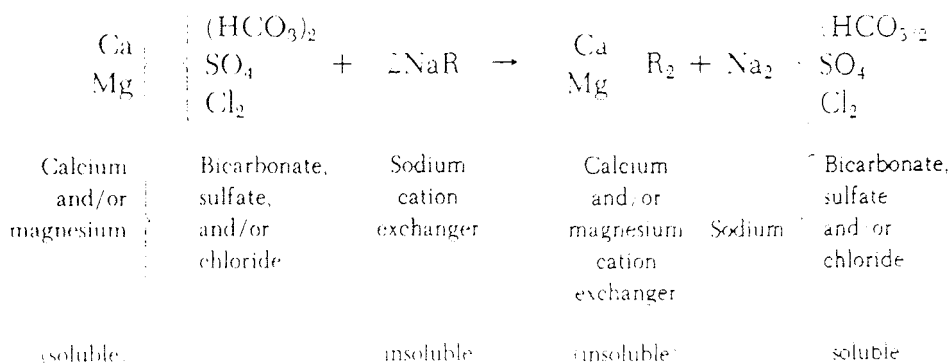
<sup>4</sup>*Soc. Chem. Ind. London Chem. Eng. Group Proc.* 54 1-6T (1935); Arden, *Water Purification by Ion Exchange*, Plenum, New York, 1968.

<sup>5</sup>*McGraw-Hill Encyclopedia of Science and Technology*, vol. 14, McGraw-Hill, New York, 1977, p. 457.

have very high exchange capacity per cubic meter of material. The next improvement was the introduction of organic ion exchangers made from sulfonated natural products such as coal, lignite, and peat. However, most high-capacity ion-exchange resins are based upon polystyrene-divinylbenzene (SDVB). Over 80 percent of ion-exchange resins are used for the treatment of water. However, the nonwater uses are of great importance and are growing. The literature covering all the versatile applications of ion exchanges is extensive.<sup>6</sup> They can be chosen to remove and purify, for example, uranium, yttrium, or streptomycin (Chap. 40) from dilute aqueous solutions, or to remove impurities from aqueous solutions, as in sugar syrup to improve crystallization, or in food technology, or for catalysts, or simply to dry nonpolar solvents.

*Sodium-cation-exchange process* is the most widely employed method for softening water.<sup>7</sup> During the softening process, calcium and magnesium ions are removed from hard water by cation exchange for sodium ions. When the exchange resin has essentially removed the calcium and magnesium ions to the limit of its capacity, the resin is regenerated to the sodium form with a salt solution in the pH range of 6 to 8. The exchange capacity of polystyrene resins is 650 kg/m<sup>3</sup> when regenerated with 250 g of salt per kilogram of hardness removed. The sodium or hydrogen-cycle cation exchangers for water treatment are usually of the styrene-divinylbenzene sulfonated synthetic resin type. This type is exceptionally stable at high temperatures (up to 150°C) and over the wide pH range of 0 to 14. In addition, it is very resistant to oxidizing conditions. The total exchange capacity is up to 925 kg of CaCO<sub>3</sub> per cubic meter of ion exchanger with a hydrogen cycle and up to 810 kg of CaCO<sub>3</sub> per cubic meter with a sodium cycle. The usual practical operating capacities are not so high.

The symbol R represents the cation-exchanger radical in the following reactions for softening:

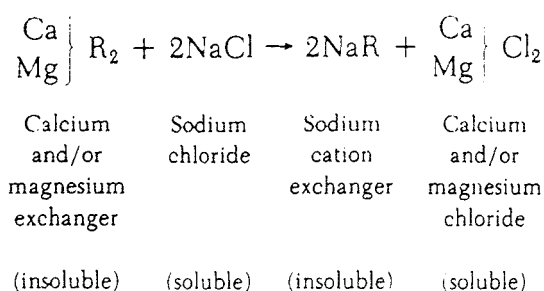


When the ability of the cation-exchange bed to produce completely softened water is exhausted, the softener unit is temporarily taken out of service, backwashed to cleanse and hydraulically reclassify the resin particles in the bed; regenerated with a solution of common salt (sodium chloride), which removes the calcium and magnesium in the form of their soluble chlorides and simultaneously restores the cation exchanger to its sodium state; rinsed free of these soluble by-products and the excess salt, and then returned to service ready to soften another equal volume of hard water. The regeneration reactions may be indicated as follows:

<sup>6</sup>ECT, 3d ed., vol. 13, 1981, p. 678; Walton, *Ion Exchange*, *Anal. Chem.* **42** (5) 86 (1970).

<sup>7</sup>Gold and Calmon, *Ion Exchange, Present Status, Needs and Trends*, AIChE Symp. Ser., vol. **76**, no. 192, p. 60, 1980, a review with 106 references.

using salt (or  $\text{H}_2\text{SO}_4$  on a hydrogen cycle):



The equipment for the process, shown in Fig. 3.2, is a large, closed cylindrical tank in which the zeolite is supported on graded gravel. The water to be softened may flow down through the tank. Auxiliary apparatus includes both brine- and salt-storage tanks. Washing and regeneration may be carried out automatically as well as manually. These softeners are installed in water lines and operated under whatever water pressure is necessary. As the exchanger bed also exerts a filtering action, any sediment from the water or from the salt must be washed off by an *efficient backwash*. This step suspends and hydraulically regrades the resin bed. The water from ion-exchange treatment usually has a hardness level of less than 1 ppm expressed as calcium carbonate. In cases where very hard bicarbonate water is encountered, it is often desirable to treat the water first by the lime process, followed by cation exchange.<sup>8</sup> The lime process actually reduces dissolved solids by *precipitating* calcium carbonate and magnesium hydroxide from the water, whereas the cation resin exchanges

<sup>8</sup>Krisher, Raw Water Treatment in the CPI, *Chem. Eng.* 85 (19) 79 (1978).

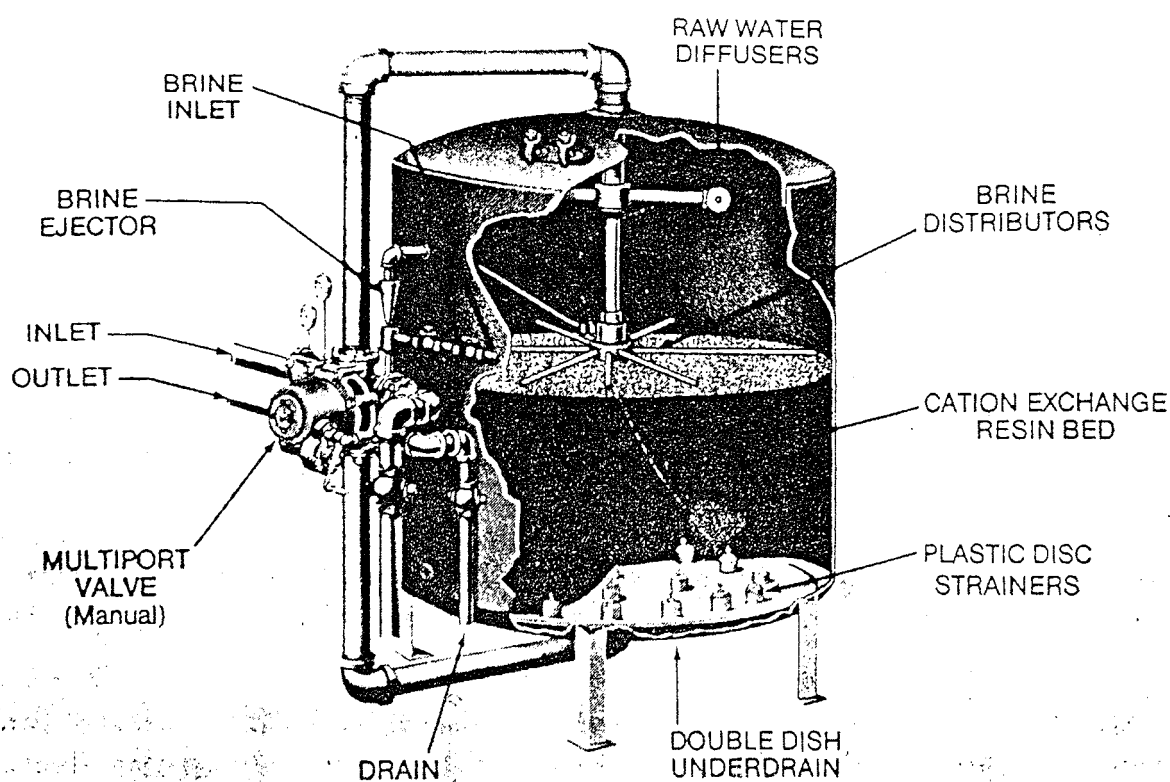
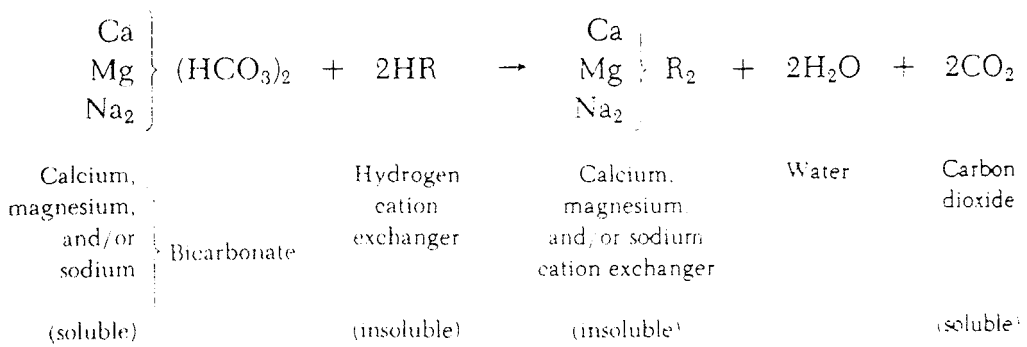


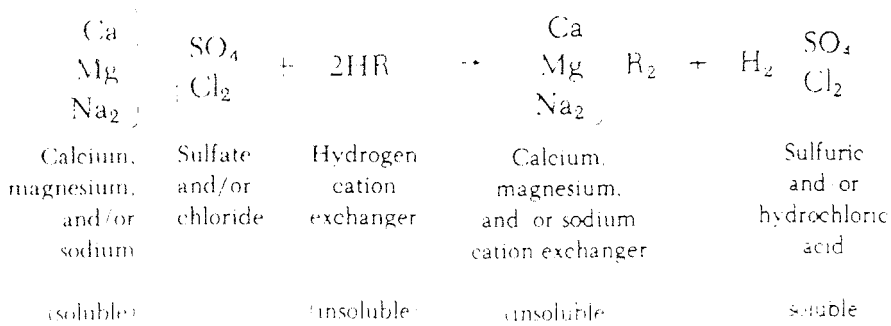
Fig. 3.2. Automatic sodium-cation-exchanger water softener. (Permutit Co.)

calcium and magnesium ions for sodium ions. The great advantage of these softeners is their convenience and the fact that they furnish water of very low residual hardness without attention or adjustment until regeneration is required even though the raw water varies in hardness from one day to the next.

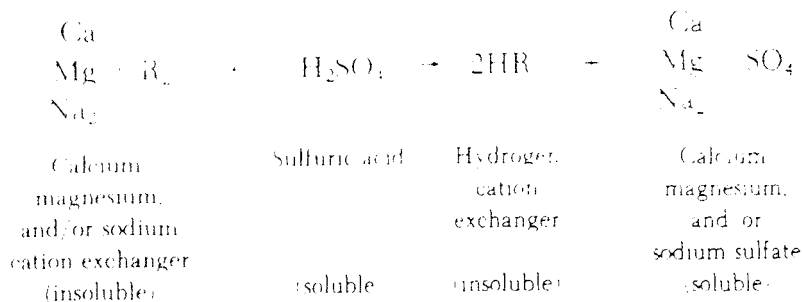
The *hydrogen-cation-exchange process* closely resembles the sodium cation procedure, except that the exchange resins contain an exchangeable *hydrogen ion* and can be employed to remove all cations. The symbol R represents the complex radical for the hydrogen-cation exchanger in the following reactions *for exchanges with bicarbonates*:



The reactions with *sulfates* and *chlorides*, using the symbol R to represent the organic radical of the exchanger, may be indicated as follows:



*Regeneration with sulfuric acid* is the most widely used and most economical method of regeneration. The reactions, in condensed form, may be indicated as follows:



Acidic water is not desirable for most purposes, and therefore the effluent from the hydrogen-cation-exchange treatment is either neutralized or blended with sodium zeolite-treated water. If demineralization is required, it is passed through an anion-exchange material, as shown in Fig. 3-3.